

# PATENT SPECIFICATION

NO DRAWINGS

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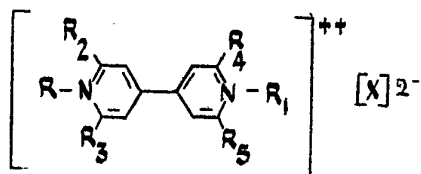
## COMPLETE SPECIFICATION

### Herbicidal Compositions

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, a British Company, of Imperial Chemical House, Millbank, London, S.W.1., do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to herbicidal compositions containing as active ingredient a substituted bipyridylium salt and to processes of combating weeds using them.

The invention provides herbicidal compositions comprising as active ingredient a 4,4'-bipyridylium quaternary salt wherein each nitrogen atom bears an aliphatic group and at least one of the four ring carbon atoms which are adjacent a nitrogen atom in the pyridine nuclei bears as a substituent an alkyl group containing from 1—4 carbon atoms; and a carrier for the active ingredient, said carrier comprising an inert solid diluent, or a liquid diluent comprising a wetting agent. The compositions preferably comprise a quaternary salt wherein the substituent alkyl group is a methyl group and it is further preferred to employ active ingredient a quaternary salt in which each pyridine nucleus bears a substituent methyl group on a ring carbon atom adjacent a nitrogen atom. The invention further provides, herbicidal compositions comprising as active ingredient a compound of the formula:



wherein R and R<sub>1</sub>, which may be the same or [Pri

different, are each alkyl groups containing from 1—4 carbon atoms, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub> and R<sub>5</sub> are groups which include at least one methyl group the remainder being either methyl groups or hydrogen atoms and X is a divalent anion or two monovalent anions; and a carrier for the active ingredient, said carrier comprising an inert solid diluent or a liquid diluent comprising a wetting agent. R and R<sub>1</sub> are preferably methyl or ethyl groups.

The anionic part of the salt may comprise for example chloride, bromide or iodide ions although [X]<sup>2-</sup> may also comprise a single divalent ion. The choice of anion depends to a large extent upon the solubility of the respective salts in water and upon the ease with which the salts can be prepared.

Symmetrical compounds of the invention can be obtained by reacting the appropriate ring—substituted 4,4'-dipyridyl with a suitable quaternising agent. Other compounds can be prepared by a similar process in which a 1-substituted -4-(4'-pyridyl)-pyridinium salt is quaternised with a suitable quaternising agent, the pyridinium salt being chosen so that its 1-aliphatic substituent is on of the aliphatic substituents required in the bipyridylium salt, and the quaternising agent is such that it introduces the required second aliphatic substituent and anion. The reaction in some instances can be carried out simply by heating the reactants together, but it is generally more convenient, especially where the process is carried out on a large scale, to have the reactants in solution or suspension in a suitable solvent or diluent.

The compositions may be in the form of concentrated compositions which is the form in which they are transported more conveniently because they contain a high proportion of the salt with a minimum of bulk. In general these compositions are diluted before

use although in certain instances, e.g. in the treatment of water weeds, this may not be necessary. Solid compositions may contain solid carriers which, depending on the use to which the compositions are to be put, may be soluble or insoluble in water. Whatever the carrier used however it should not act as a base exchange material or if soluble in water, form strongly alkaline solutions because a carrier having either property may cause partial or complete de-activation of the salt. Suitable solid carriers include magnesium sulphate, sodium sulphate, sodium acetate, potassium dihydrogen phosphate, potassium chloride, citric acid and urea. Since dry free flowing compositions are generally more convenient to handle than pastes, especially good solid compositions may be obtained by adding sufficient of an aqueous solution to the salt to a partially dehydrated salt, e.g. partially dehydrated magnesium sulphate, so that after addition has been made a solid composition is obtained which is either dry or else requires little drying. Compositions containing a soluble solid carrier may be used merely by dissolving the solids in water and then applying the resulting solution in the normal way. Solid compositions containing insoluble carriers may incorporate as a carrier vermiculite, cellulose ethers and magnesium carbonate. These compositions may preferably be applied in the form of dry substantially dust-free granules.

In general very satisfactory compositions are obtained using a liquid carrier which, usually comprises water on account of its cheapness and suitability. Such compositions whether concentrated or dilute include a wetting agent which, as in the case of the carrier, should not affect adversely the herbicidal properties of the salt. Wetting agents which are especially satisfactory include condensation products of ethylene oxide with substance having a hydrogen capable of reacting with the ethylene oxide, e.g. alkylated phenols, e.g. octyl phenol and nonyl phenol, sorbitan monolaurate, oleyl alcohol and cetyl alcohol. The amount of wetting agent which can be used may vary widely. For example concentrated compositions may contain from 5 to 15% by weight, while the proportions present in the dilute compositions may contain from 0.01—0.05% by weight. In either case however there are occasions when smaller or larger amounts may be used.

The amount of herbicidal salt which may

Found:  $C_{14}H_{18}N_2I_2$  requires:

#### EXAMPLE 2

1,2,6,1',2',6' - Hexamethyl - 4,4' - bipyridylum diiodide was prepared by the process of Example 1 above, but using a molar equivalent amount of 2,6,2',6' - tetramethyl -

be used in the compositions may also vary considerably. For concentrated compositions which may require dilution before use from 5 to 70% by weight is generally very satisfactory, whilst diluted compositions which generally are more suitable for application without further treatment usually contain from 0.002 to 2.00% by weight of the salt.

The compositions may also contain other ingredients known to the art as being suitable in the formulation of herbicides, e.g. dispersing agents, binders, stickers, corrosion inhibitors, stabilising and colouring agents. Since the compounds tend to be corrosive, especially in aqueous solution, the presence of a corrosion inhibitor is sometimes especially advantageous. Suitable inhibitors include water soluble phosphates which in aqueous solution liberate  $H_2PO_4^-$  ions, e.g. potassium dihydrogen phosphate and sodium dihydrogen phosphate. Other inhibitors which may be used are sodium molybdate, sodium metaborate and sodium benzoate.

The compositions may be applied in the usual way normally employed for applying herbicides. Solid granules or liquid compositions may be distributed in rivers, or canals to destroy water weeds and ordinary spray equipment may be used in the application of liquid compositions to weeds growing on land. The time taken for the composition to take effect varies according to the nature of the weed population, the conditions prevailing at the time of application and the amount of salt applied. In general however, most forms of weeds are either killed or severely damaged within a period of 14 days.

The invention is illustrated by the following Examples.

#### EXAMPLE 1

This Example describes the preparation of 1,2,1',2' - tetramethyl - 4,4' - bipyridylum diiodide.

2,2' - Dimethyl - 4,4' - bipyridyl (3 g.) was heated under reflux in 90% ethanol (50 ml) with methyl iodide (5.5 ml) for six hours. The crystals which had separated were then collected and recrystallised from dilute ethanol, yielding 1,2,1',2' - tetramethyl - 4,4' - bipyridylum diiodide as a solid product. An attempt to take the melting point of this product was unsuccessful as it did not melt below 320°C. The analysis of the product was as follows:—

Found: C, 35.1; H, 3.8; N, 6.2%  
C, 35.9; H, 3.8; N, 6.0%

4,4' - bipyridyl instead of 2,2' - dimethyl - 4,4' - dipyridyl. The product was obtained as a solid having no definite melting point but decomposes slowly from 280°C upwards. The product had the following analysis:—

Found: C, 37.3; H, 4.45; N, 5.8%  
 $C_{16}H_{22}N_2I_2$  requires: C, 38.7; H, 4.4; N, 5.6%

## EXAMPLE 3

1,2,6,1' - Tetramethyl - 4,4' - bipyridylum  
 5 diiodide was prepared by the process of Example 1, but using a molar equivalent amount of 2,6 - dimethyl - 4,4' - bipyridyl instead

of 2,2' - dimethyl - 4,4' - bipyridyl. The product was obtained as a solid, m.p. 310°C (decomp.) which had the following analysis:— 10

Found: C, 35.0; H, 2.7; N, 6.25%  
 $C_{14}H_{13}N_2I_2$  requires: C, 35.9; H, 3.85; N, 6.0%

The invention also includes compounds in  
 15 which the aliphatic substituents on the nitrogen atoms of the 4,4' - bipyridyl nucleus are N-substituted carbamoyl alkyl radicals, and the following Example describes the preparation of such a compound.

## EXAMPLE 4

2,2' - Dimethyl - 4,4' - bipyridyl (5 g.)

was heated under reflux with N,N - diethyl - 2 - chloracetamide (8.6 g.) at 140°C for one hour. The resulting solid product obtained on cooling the reaction mixture was recovered and recrystallised from ethanol, yielding 1,1' - bis(diethyl - carbamoylmethyl) - 2,2' - dimethyl - 4,4' - bipyridylum dichloride monohydrate. The analysis of the products was as follows:— 25 30

Found: C, 57.7; H, 8.0; N, 10.2%  
 $C_{24}H_{36}O_2N_4Cl_2 \cdot H_2O$  requires: C, 57.4; H, 7.6; N, 11.3%

## EXAMPLE 5

Aqueous solutions were made containing  
 35 varying proportions of 4,4' - bipyridylum salts the preparations of which are described in Examples 1—3 and 0.1% by weight of a wetting agent sold under the trade name 'Lissapol' NX, 'Lissapol' being a registered trade mark. The wetting agent comprised a condensation product of ethylene oxide and nonyl phenol to which had been added 10% by weight of iso-propanol.

The solutions were then sprayed into a  
 45 number of dicotyledons including sugar beet, mustard, kale, clover, mayweed and red-shank. A number of monocotyledons, namely barley, cocks foot, wheat and wild oats were similarly treated. It was found that after 14 days all the plants were either killed or severely damaged when treated at the rate of 2 lb and 10 lb per acre of active compound. The amount of salt in the solutions corresponded to solutions containing 0.02 and 0.1% by weight of salt respectively. 50 55

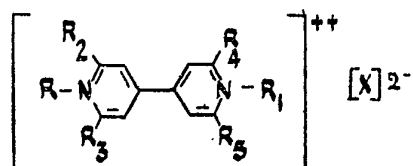
## WHAT WE CLAIM IS:—

1. A hebicidal composition comprising as active ingredient a 4,4' - bipyridylum quaternary salt wherein each nitrogen atom bears an aliphatic group and at least one of four ring carbon atoms which are adjacent a nitrogen atom in the pyridine nuclei bears as a substituent an alkyl group containing from 1—4 carbon atoms; and a carrier for the active ingredient, said carrier comprising an inert solid diluent, or a liquid diluent comprising a wetting agent.

2. A herbicidal composition according to Claim 1 wherein the alkyl group is a methyl group. 70

3. A herbicidal composition according to either of claims 1 or 2 wherein each pyridine nucleus bears at least one substituent methyl group on a ring carbon atom adjacent a nitrogen atom. 75

4. A herbicidal composition comprising as active ingredient a 4,4' - bipyridylum quaternary salt having the formula:—



wherein R and  $R_1$ , which may be the same or different, are each alkyl groups containing from 1—4 carbon atoms,  $R_2$ ,  $R_3$ ,  $R_4$  and  $R_5$  are groups which include at least one methyl group the remainder being either methyl groups or hydrogen atoms and X is a divalent anion or two monovalent anions; and a carrier for the active ingredient, said carrier comprising an inert solid diluent, or a liquid diluent comprising a wetting agent. 80 85

5. A herbicidal composition according to Claim 4 wherein R and  $R_1$  each represents a methyl or an ethyl group. 90

6. A herbicidal composition according to any one of the preceding Claims wherein the carrier comprises a mixture of water and a wetting agent. 95

7. A herbicidal composition according to Claim 6 containing from 5 to 70% by weight of salt.

8. A herbicidal composition according to any one of the preceding Claims containing from 5 to 15% by weight of wetting agent. 100

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9. A herbicidal composition according to any one of the preceding Claims containing a corrosion inhibitor.
10. A herbicidal composition according to any one of Claims 1 to 6 and 9 containing from 0.002 to 2.00% by weight of salt.
11. A process of combating weeds comprising treating weeds with a composition according to any one of the preceding claims.
12. A herbicidal composition as hereinbefore described, with particular reference to Example 5.
13. A process of combating weeds as hereinbefore described with particular reference to Example 5.
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- WALTER SCOTT,  
Agent for the Applicants.

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